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Molecular Evolution in Protobiological Systems, including a Search for Catalysts and Catalytic Activity in the Intermediate Systems which form During the Syntheses of Low Molecular Weight Organic Compounds.

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Molecular Evolution Project

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Since this is the first semiannual period of a proposed three years' program, most of the effort has gone into the design of experiments and the construction of special items of apparatus. An attempt has been made to relate the problem of molecular evolution to the question of the origin of life. For the benefit of students and staff, a seminar series on the origin of life was held and, although not a part of this project, a description is given in the enclosure.

Remarks on the Molecular Evolution Problem

Some of the features of molecular evolution which have recently become apparent to us will be noted briefly here, and described more fully in subsequent publication. Our initial approach has been by means of attempted generalizations of the Miller experiment. It seems important to be able to comment on the extent to which a Miller type synthesis is independent of starting materials and type of energy source, since the relevance of any given experiment to actual primeval earth conditions may be questioned.

Such a generalization may be stated in the following way: consider a closed system containing a defined but arbitrary chemical mixture which is subjected to a given energy flux of sufficient quantum energy to break any chemical bonds in the system, if it is absorbed. One may then ask whether such a system will 1) approach an equilibrium, or 2) approach a steady state? It might seem that only under highly special conditions would an equilibrium be attained, but that a steady state should result quite generally. What then would be the properties of such a steady state? As molecular evolution proceeds in the presence of this energy flux, will there be a tendency toward the formation of higher molecular weight compounds or toward simpler compounds? These questions can of course be approached experimentally.

Then there is the question of homogeneous vs. heterogeneous systems. The Miller experiment itself is heterogeneous: the whole synthesis eventually comes to a halt as the gaseous starting materials are removed from the reaction through conversion to larger molecules which remain in the acqueous phase and are unable to reach the electrical discharge and react further. There is thus a built-in mechanism for the protection of newly synthesized materials against dissolution by the discharge. The price paid for this is the inability to further excite these compounds to undergo further synthesis.

It may be pointed out that most of the detailed mechanisms proposed to have occurred during the origin of life require special conditions, e.g. Fox's anhydrous amino acid reactions, Oparin's coacervate formation, Oro's cyanide syntheses, etc. That is to say, all of these require heterogeneous systems and reactants in high concentrations. When such highly specialized experimental conditions are invoked, the burden of proof is upon the proposer, to show that such conditions are historically realistic.

Molecular evolution in homogeneous (or "almost-homogeneous") systems seems to have been largely ignored. The basis for this appears to be the belief that closed chemical systems under excitation will tend toward simpler molecules. Experimental data regarding such systems is meager, but that which is available from radiation chemical studies suggests that continued molecular aggregation may occur. For example, in the radiolysis of methane the main product is hydrogen, but ethane, propane, etc., are formed in smaller yields. Polymers are also found. If one then starts with a given saturated hydrocarbon one would expect to find a distribution of products of both lower and higher m.w. The nature (or even existence) of steady state composition has not to our knowledge been investigated. Since molecular evolution in homogeneous systems requires the least number of special assumptions, the data obtained should have general applicability.

The "Imprint Hypothesis"

Since the greatest source of energy available for prebiological synthesis was the solar output, we are presently engaged in a study of molecular evolution under U.V. irradiation. One quite general hypothesis has emerged which is now being experimentally tested. The idea is quite simple: if one irradiates a solution of a complex organic mixture with monochromatic U.V. of wavelength λ, then those molecules which absorb appreciably at this wavelength will be preferentially converted to photo products, while those not absorbing at this wavelength will remain unaltered. The absorption spectrum of the system will thus show a dip in O.D. at the wavelength of the incident energy. By extension therefore, if one irradiates simultaneously at several λ's, the absorption spectrum of the mixture should eventually show depressions at these λ's. This may be summarized by saying that the irradiation of an organic solution with U.V. having a given spectral profile will induce photochemical changes such that the solution will eventually have an absorption spectrum which is the complement of the spectrum of the incident light. This, we term the "imprint hypothesis".

If this hypothesis proves valid, then we can at once say something about the steady state of a molecular evolution process - namely that though we may know very little about the chemical composition of the system, it will tend toward such a distribution of molecular types as to minimize its interaction with the incident light flux. Or, in another context, if the distribution of solar energy on the earth's surface during its primeval stages be known, one can say something about the relative stabilities of the different biological compounds under these conditions. The experimental evaluation of this hypothesis is in progress.

Experiments in Progress

We are investigating the reaction of simple hydrocarbon gases in an electric discharge, by means of gas chromatography, in order to determine the nature of the products and to see whether this form of excitation leads to similar results as ionizing radiation. Photochemical experiments involving the irradiation of fairly complex organic solutions with monochromatic ultraviolet radiation have been started and preliminary results seem to support the imprint hypothesis. Two experiments involving the irradiation of a mixture of aqueous amino acids with Co^{60} γ-rays, were carried out to fairly high total doses ($\sim 10^8$ rads) and the osmolarity of the solution was determined as a function of dose. It was found in both instances that there was an intermediate rise in osmolarity - indicating an increase in the number of product molecules, followed at higher doses by a decrease. It is hoped that the further study of these systems will reveal whether some colligative property may be followed as an indicator of whether chemical bond formation or destruction is the dominating feature in a given system.

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BIOPHYSICS SEMINAR SERIES

Spring Quarter 1962

The Biophysics Laboratory is sponsoring a series of seminars on the subject of "The Origin of Life". These will be held in Room ph 104 (Physics Lecture Building) on Thursday afternoons at 4:15 P.M.

April 19	Dr. M. S. Blois, Biophysics Laboratory, Stanford University "The Experimental Method and the Origin of Life Problem"
April 26	Dr. Carl Sagan, Department of Astronomy, University of California, Berkeley "Organic Matter and the Early History of the Solar System"
May 3	Dr. Sidney W. Fox, Institute for Space Biosciences, Florida State University "Laboratory Tests of Concepts of Abiogenesis"
May 10	Dr. Stanley L. Miller, University of California, San Diego "The Synthesis of Organic Compounds on the Primitive Earth"
May 17	Dr. Konrad Krauskopf, School of Mineral Sciences, Stanford University "The Geochemical Background for the Origin of Life"
May 24	Dr. A. P. Kimball, Stanford Research Institute "Pathway of Adenine Synthesis under Possible Primitive Earth Conditions"

Biophysics Laboratory
Stanford University
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